

# Degradation of Mecoprop at Different Concentrations in Surface and Sub-surface Soil

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**Abstract:** Biodegradation of [*ring*- $^{14}\text{C}$ ] mecoprop (2-(4-chloro-2-methylphenoxy) propionic acid) was determined in surface and sub-surface soil at concentrations of 0.0005, 0.05, 0.5, 5, 50, 500, 5000 and 25 000  $\text{mg kg}^{-1}$ .

The kinetics of mineralisation were evaluated from the mineralisation rates as a function of time and by non-linear regression analysis.

In the sub-surface soil, degradation was 6–8 times slower than in surface soil, but the shape of the curves was the same in both layers.

At concentrations between 0.0005 and 0.5  $\text{mg kg}^{-1}$ , in both surface and sub-surface soil, degradation was initially zero-order followed by first-order kinetics. At 5 to 500  $\text{mg kg}^{-1}$  in surface soil and 5 to 50  $\text{mg kg}^{-1}$  in sub-surface soil the degradation rate was initially either constant or decreasing followed by exponential degradation indicating increasing populations of mecoprop decomposers in the soil. At 5000 and 25 000  $\text{mg kg}^{-1}$  in the surface soil and at 500, 5000 and 25 000  $\text{mg kg}^{-1}$  in the sub-surface soil, the degradation was negligible, as determined by the percentage [ $^{14}\text{C}$ ] carbon dioxide evolved.

By non-linear regression, the three-half order model was found to describe the mineralisation. © 1998 SCI

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Key words: mecoprop; degradation; mineralisation; kinetics; surface soil; sub-surface soil

## 1 INTRODUCTION

Pesticides may appear in a wide range of concentrations in soil and they have been reported in ground water since the middle of the eighties in most western countries.<sup>1</sup> In Danish groundwater, pesticides have been found at concentrations between 0.01 and 25  $\mu\text{g litre}^{-1}$ . The low concentrations were considered to be a result of ordinary agricultural use, whereas the high concentrations most likely came from point-sources, where concentrations close to the water solubility may appear in soil pore water.<sup>2,3</sup>

The present laboratory study examines the degradation of mecoprop (2-(4-chloro-2-methylphenoxy)propionic acid) at a wide range of concentrations in both

surface and sub-surface soils by simulating degradation from the point source and outwards.

The herbicide mecoprop, which is used widely to control broad-leaved weeds in cereals in the autumn and spring, is used in this study, since it is often found in Danish groundwater.

The potassium salt of mecoprop is highly soluble in water (795  $\text{g litre}^{-1}$ ) and sorption to soil is low (the distribution coefficient between soil and water,  $K_d$ , is between 0.07 and 0.20  $\text{litre kg}^{-1}$  at a mecoprop concentration of 5  $\text{mg litre}^{-1}$ ).<sup>4,5</sup>

Degradation of mecoprop is mainly microbial and some micro-organisms are able to grow on mecoprop as a sole carbon source.<sup>6–9</sup>

The time for 50% degradation of mecoprop in surface soil, at concentrations of 2–5  $\text{mg kg}^{-1}$ , has been reported as one to eleven days.<sup>5,7,10</sup> At concentrations higher

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than 5 mg kg<sup>-1</sup> the time for 50% degradation increases with the concentration from six days at 10 mg kg<sup>-1</sup> to 42 days at 250 mg kg<sup>-1</sup>.<sup>10</sup>

No degradation studies of mecoprop at very low and very high concentrations in surface and sub-surface soil have been reported. A study of the phenoxyacid 2,4-D showed no degradation over 80 days at concentrations higher than 500 mg kg<sup>-1</sup> in soils with an organic matter content of 0.9%. If the organic matter was 3.9%, degradation was observed even at 20 000 mg kg<sup>-1</sup>.<sup>11</sup>

The time interval for 50% disappearance of mecoprop in sub-surface soil is five to ten times longer than in surface soil at a concentration of 2 mg kg<sup>-1</sup>.<sup>5</sup>

## 2 EXPERIMENTAL METHODS

### 2.1 Chemicals and soils

Uniformly *ring*-<sup>14</sup>C-labelled mecoprop (potassium salt), with a specific activity of 6.88 MBq mg<sup>-1</sup> and radiochemical purity of 98% (Amersham) was used in different ratios, together with unlabelled mecoprop (M-propionat-50 potassium salt from Esbjerg Kemi, Denmark) at a concentration of 589 g litre<sup>-1</sup>.

Soil samples were from the Danish Experimental Farm, Flakkebjerg. The soil had not been treated with mecoprop for two years prior to sampling. Surface soil was collected at a depth of 0–30 cm and sub-surface soil at a depth of 40–60 cm. After sampling, the soils were dried at room temperature to a water content of about 25% of total water holding capacity (WHC). The soils were sieved (<2 mm) and stored at 5°C for about a week until use. Table 1 shows the composition of the soils.

### 2.2 Experiment and incubation

Aqueous mixtures of unlabelled and [<sup>14</sup>C]mecoprop were added *via* pipette to each flask (duplicate), containing dry soil (50 g), to obtain total concentrations of

0.0005, 0.05, 0.5, 5, 50, 500, 5000 and 25 000 mg mecoprop (potassium salt) per kg of dry soil. The aqueous mixtures consisted of 1 ml labelled mecoprop and different amounts of unlabelled solution, except that at 0.0005 and 0.05 mg kg<sup>-1</sup>, labelled mecoprop only was used. Each duplicate flask contained about 10<sup>6</sup> dpm, except for flasks with concentration 0.0005 mg kg<sup>-1</sup>, which contained about 10<sup>4</sup> dpm. After addition of chemical, water was added in order to adjust to 50% of WHC and the flasks were incubated at 15°C. The water content was adjusted every second week during the incubation period. The <sup>14</sup>C evolved as carbon dioxide was trapped by passing a slow stream (6–8 ml min<sup>-1</sup>) of carbon dioxide-free atmospheric air through the flasks and then through one glycerol absorber to absorb organic compounds and two potassium hydroxide absorbers (10 ml, 1 M in each absorber) to absorb carbon dioxide. Radioactivity was determined using a Liquid Scintillation Counter LKB-WALLAC 1215 Rackbeta II and Ultima Gold (Packard) as the scintillation liquid.

To check whether the degradation was microbial, flasks with sterilised surface and sub-surface soil, at a concentration of 5 mg kg<sup>-1</sup> mecoprop, were incubated as described above. The soil was irradiated (11 kGy) and the air was filtered through 0.2 µm mesh filters before entering the incubation flasks.

### 2.3 Residue analysis

After the termination of incubation the test vessels, [<sup>14</sup>C]mecoprop was extracted from soil by sonication twice in water and calcium hydroxide (250 ml + 5 g), followed by centrifugation. The combined extracts were acidified to pH < 2 with hydrochloric acid and passed through an activated C-18 filter (SPE). The filter was extracted with methanol (2 × 10 ml). The extract was evaporated to dryness under nitrogen and dissolved in the mobile phase, methanol + tetrabutylammonium-hydrogensulfate (2 + 1 by volume; 1 ml; Fomsgaard, I., 1996, pers. comm.). After HPLC (Waters Associates) on

TABLE 1  
Properties of the Soils and Sorption of Mecoprop Expressed as  $K_d$

Depth (cm)	Clay <sup>a</sup> (%)	Silt <sup>a</sup> (%)	Sand <sup>a</sup> (%)	Humus <sup>b</sup> (%)	pH	WHC <sup>c</sup>	Sorption <sup>d</sup> (litre kg <sup>-1</sup> )		
							$K_{d, 5}$	$K_{d, 500}$	$K_{d, 5000}$
0–30	14.3	17.7	65.2	2.9	6.1	50	0.56	0.34	0.25
40–60	22.9	11.1	65.7	0.3	6.5	35	0.11	0.11	0.13

<sup>a</sup> Clay: <0.002 mm, silt: 0.002–0.02 mm, sand: 0.02–2 mm.

<sup>b</sup> Humus: %C × 1.72.

<sup>c</sup> WHC: water holding capacity in g water per 100 g dry soil.

<sup>d</sup> Sorption:  $K_{d, 5}$ ,  $K_{d, 500}$  and  $K_{d, 5000}$  are the distribution coefficients for mecoprop at 5, 500 and 5000 mg kg soil<sup>-1</sup> (5 g soil in 25 ml 0.01 M CaCl<sub>2</sub>), respectively.

ODS-2 at a flow of  $0.4 \text{ ml min}^{-1}$ , the eluate was collected in fractions (1 ml) for measurement of radioactivity and determination of mecoprop.

Residual activity in the extracted soil was determined by combustion on an oxidiser (Packard). The  $[^{14}\text{C}]$ carbon dioxide, evolved after combustion was trapped in Carbosorp and Permafluor (Packard) and counted by scintillation.<sup>5</sup>

## 2.4 Kinetics

Kinetics can be divided in two categories: degradation with and without growth of the micro-organisms. Degradation without growth may obey zero- or first-order kinetics. The method used to elucidate the kinetics of mineralization data was to plot mineralisation rate versus time on a semi-logarithmic scale. If degradation follows first-order kinetics, the plot gives a straight line with a slope less than 0. A horizontal line describes zero-order kinetics. An increase in mineralisation rate is often due to growth of the degrading micro-organisms.

Another method to investigate the kinetics is to perform non-linear regression analysis on  $[^{14}\text{C}]$ carbon dioxide evolution data by a curve-fitting program.

The three-half order model has been proposed as a model to describe the mineralisation of xenobiotic substances in soil.<sup>12</sup> The linear and exponential forms of the three-half order model describing the mineralisation to the product, carbon dioxide ( $P$  in the equations), are given by:

$$P = S_0 \times [1 - \exp(-k_1 t - \frac{1}{2} k_2 t^2)] + k_0 t \text{ (linear)} \quad (1)$$

and

$$P = S_0 \times \{1 - \exp[-k_1 t - E_0/\mu \times (\exp(\mu t) - 1)]\} + k_0 t \text{ (exponential)} \quad (2)$$

where  $S_0$ : amount of substrate converted to carbon dioxide;  $k_0$ : zero order rate constant;  $k_1$ : constant in units of reciprocal time;  $k_2$ : constant in units of reciprocal time squared;  $\mu$ : growth rate constant and  $E_0$ : initial cell concentration. In the linear form  $k_2$  becomes zero when there is no growth of the biomass, which leads to first-order kinetics.

These models are used to study the mineralisation data. Non-linear regression analysis was carried out by the curve-fitting program Gnufit (Gnuplot MS-DOS version 3.5).

## 3 RESULTS

### 3.1 Evolution of $[^{14}\text{C}]$ carbon dioxide from $[ring-^{14}\text{C}]$ mecoprop

Figures 1 and 2 show the total evolution of  $^{14}\text{C}$  as carbon dioxide (the sum curves of individual test vessels

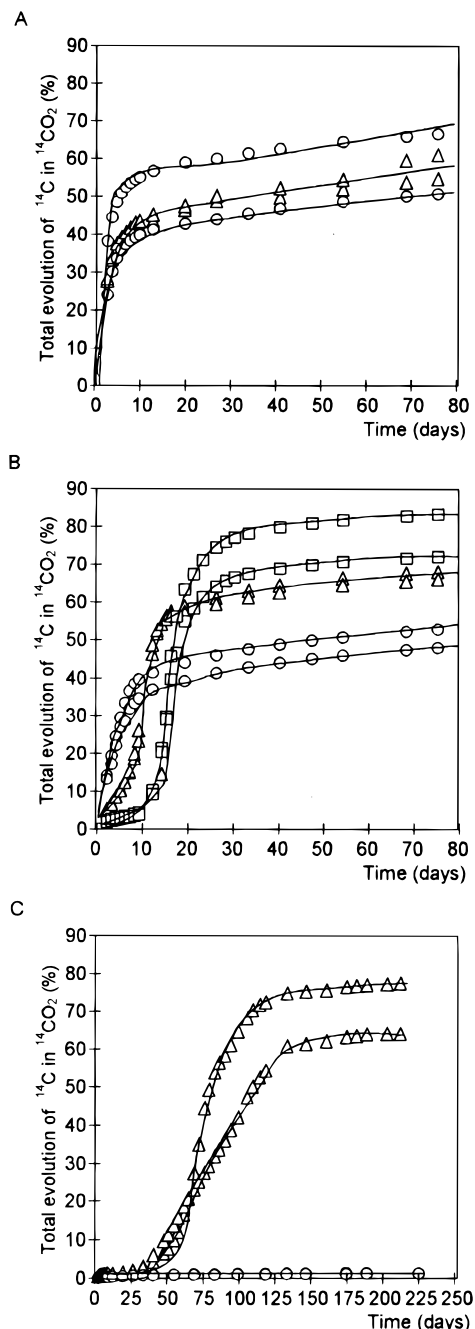
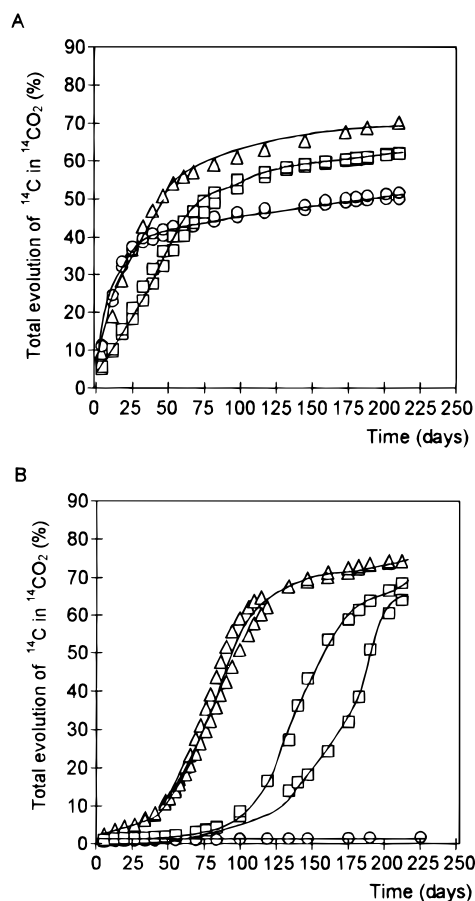


Fig. 1. Sum-curves indicating total evolution of  $^{14}\text{C}$  as carbon dioxide from the different concentrations of  $[^{14}\text{C}]$ mecoprop in surface soil. A: ( $\Delta$ )  $0.0005$ , ( $\circ$ )  $0.05 \text{ mg kg}^{-1}$ . B: ( $\circ$ )  $0.5$ , ( $\Delta$ )  $5$ , ( $\square$ )  $50 \text{ mg kg}^{-1}$ . C: ( $\Delta$ )  $500$ , ( $\circ$ )  $5000 \text{ mg kg}^{-1}$ .

expressed as percentage of applied rate) from the different concentrations of  $[^{14}\text{C}]$ mecoprop in surface and in sub-surface soil. The figures also show the curves fitted to the determined values according to eqns (1) and (2) (linear and exponential, respectively). The evolution of carbon dioxide at  $25000 \text{ mg kg}^{-1}$  in the surface soil and  $5000$  and  $25000 \text{ mg kg}^{-1}$  in the sub-surface soil is less than 1% and is therefore not shown in the figures.



**Fig. 2.** Sum-curves indicating total evolution of  $^{14}\text{C}$  as carbon dioxide from different concentrations of  $[^{14}\text{C}]$ mecoprop in sub-surface soil. A: ( $\Delta$ ) 0.0005, ( $\circ$ ) 0.05, ( $\square$ ) 0.5  $\text{mg kg}^{-1}$ . B: ( $\Delta$ ) 5, ( $\square$ ) 50, ( $\circ$ ) 500  $\text{mg kg}^{-1}$ .

For both soils, at concentrations of 0.0005 and 0.05  $\text{mg kg}^{-1}$ , the first-order equation was fitted to the mineralisation curves (Figs 1A and 2A). Fitting to the linear form of the three-half order model was also tried, but  $k_2$  became negative.

The linear form of the three-half order model gave the best fit of results of the mineralisation data at 0.5  $\text{mg kg}^{-1}$  in both soils (Figs 1B and 2A).

At concentrations of 5  $\text{mg kg}^{-1}$  and higher (Figs 1B, 1C and 2B) the mineralisation curves were S-shaped and therefore the exponential form of the three-half order model gave good results at 5  $\text{mg kg}^{-1}$  (Figs 1B and 2B).

At higher concentrations it was not possible to find one single equation which fitted all the data points. The curve was therefore divided into two parts.

At 50  $\text{mg kg}^{-1}$ , in the surface soil, the exponential form gave the best fit to the data points during the first 20 days (Fig. 1B). Thereafter the data points fitted well to the linear form.

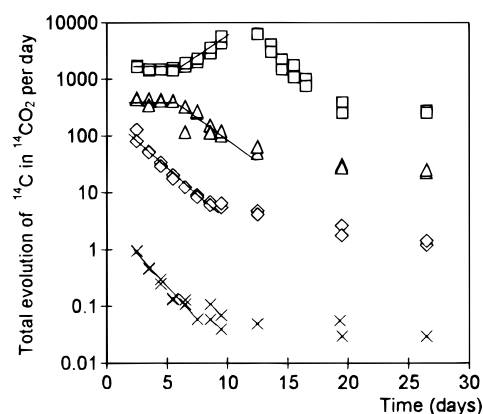
At 50  $\text{mg kg}^{-1}$  in the sub-surface soil, and at 500  $\text{mg kg}^{-1}$  in the surface soil, the exponential form gave the best fit in the beginning. Later the data followed first-order kinetics (Figs 1C and 2B).

### 3.2 Ring-carbon evolved per day

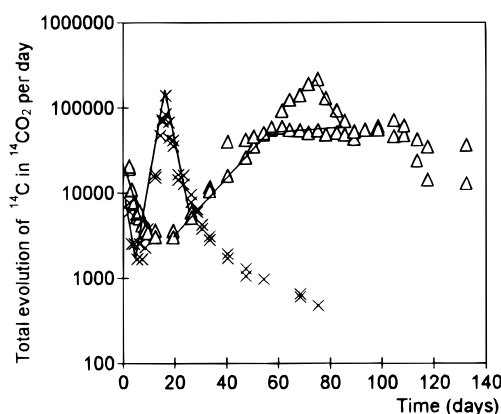
Rate of degradation can also be expressed as the ring-carbon evolved as carbon dioxide per day. Figures 3 and 4 show the daily evolution of ring carbon from the surface soil on a semi-log scale. The mineralisation rate constants and the correlation coefficients for the surface and sub-surface soil are shown in Tables 2 and 3. Earlier studies showed that half of the  $[^{14}\text{C}]$ mecoprop (2  $\text{mg kg}^{-1}$ ) was degraded when 12%  $^{14}\text{C}$  was evolved as  $[^{14}\text{C}]$ carbon dioxide.<sup>5</sup> Tables 2 and 3 show the number of days elapsed before 12%  $[^{14}\text{C}]$ carbon dioxide was evolved. This approximates to the degradation rate.

The degradation of mecoprop at concentrations of 0.0005, 0.05 and 0.5  $\text{mg kg}^{-1}$  in surface soil followed zero-order kinetics during the first three days (Table 2, curves not shown). After this the degradation rate decreased.

At 5  $\text{mg kg}^{-1}$ , zero-order kinetics appeared from day one to day three. The mineralisation rates at 5, 50 and 500  $\text{mg kg}^{-1}$  were identical, in that an initial decrease in rate was followed by an increase. The duration of increasing degradation rate increased with the concentration. There was a difference between the two repli-



**Fig. 3.** Ring-carbon evolved per day from surface soil at ( $\times$ ) 0.0005, ( $\diamond$ ) 0.05, ( $\Delta$ ) 0.5, ( $\square$ ) 5  $\text{mg kg}^{-1}$  mecoprop.



**Fig. 4.** Ring-carbon evolved per day from surface soil at mecoprop concentrations of ( $\times$ ) 50, ( $\Delta$ ) 500  $\text{mg kg}^{-1}$ .

**TABLE 2**  
Mineralisation Constants (*k*) and Correlation Coefficients (*r*) for Degradation of Mecoprop in Surface Soil at Six Different Concentrations

Concn (mg kg <sup>-1</sup> )	Zero-order kinetics		First-order kinetics			No. of days until 12% <sup>14</sup> C <sub>2</sub> was evolved
	Period (days)	r	Period (days)	k	r	
0.0005	0–2.9	0.9843	2.5–7.5	0.5228	0.9575	1
0.05	0–2.9	0.9891	2.5–8.5	0.4490	0.9851	1
0.5	0–2.9	0.9862	5.5–13.6	0.2927	0.9437	2
	2.5–5.5	0.9709				
5	0–2.9	0.9829	—			7
	2.5–6.5	0.9980				
50	—		2.5–5.5 <sup>a</sup>	0.4200	0.9019	14
500	—		2.5–7.5 <sup>a</sup>	0.2897	0.9531	50–56

<sup>a</sup> Not full first-order kinetics—see text.

cates at 500 mg kg<sup>-1</sup>. One of them followed the pattern as described above, but the other followed zero-order kinetics for a few days after an initial increase in mineralisation rate.

At 50 and 500 mg kg<sup>-1</sup> the initial decrease in rates is not pure first-order kinetics because the evolution of

carbon dioxide is very small (< 10%)—see Figs. 1B and 1C. The decrease may be caused by lethal effects of mecoprop on the micro-organisms.

At 5000 and 25000 mg kg<sup>-1</sup>, the degradation rates (not shown) decreased in the first 50 days but after that the rates were almost constant. The evolution of carbon

**TABLE 3**  
Mineralisation Constants (*k*) and Correlation Coefficients (*r*) for Degradation of Mecoprop in Sub-surface Soil at Five Different Concentrations

Concn (mg kg <sup>-1</sup> )	Zero-order kinetics		First-order kinetics			No. of days until 12% <sup>14</sup> C <sub>2</sub> was evolved
	Period (days)	r	Period (days)	k	r	
0.0005	5.5–26.4	0.9995	26.4–98.6	0.0345	0.9295	8
0.05	—		12.7–40.5	0.0809	0.9504	6
0.5	5.5–54.5	0.9906	54.5–98.6	0.0228	0.9832	16
5	—		—			50
50	—		—			108–125

**TABLE 4**  
Recovery of <sup>14</sup>C after Degradation of [<sup>14</sup>C]Mecoprop in Surface Soil at Six Different Concentrations and in Sterile Soil at 5 mg kg<sup>-1</sup>

Concn (mg kg <sup>-1</sup> )	<sup>14</sup> C (%) (±SD)			Total recovery of <sup>14</sup> C (%) (±SD)
	KOH	Extract	Extracted soil	
0.0005 <sup>a</sup>	57.9 (±3.2)	ND <sup>c</sup>	25.5 (±4.3)	83.3 (±4.4)
0.05 <sup>a</sup>	58.6 (±7.9)	3.2 (±0.2)	49.3 (±1.6)	111.1 (±8.0)
0.5 <sup>a</sup>	50.5 (±2.5)	3.1 (±0.05)	43.0 (±2.2)	96.6 (±2.9)
5 <sup>a</sup>	67.1 (±1.0)	2.1 (±0.1)	33.6 (±3.2)	102.8 (±2.5)
5, sterile <sup>a</sup>	1.9 (±0.4)	63.4 (±0.9)	30.7 (±2.4)	96.0 (±2.0)
50 <sup>a</sup>	77.6 (±5.6)	1.6 (±0.2)	20.7 (±2.1)	99.8 (±5.8)
500 <sup>b</sup>	70.8 (±6.7)	5.2 (±0.7)	22.0 (±2.6)	98.0 (7.0)

<sup>a</sup> Incubated for 76 days.

<sup>b</sup> Incubated for 211 days.

<sup>c</sup> ND = Not determined.

**TABLE 5**  
Recovery of  $^{14}\text{C}$  after Degradation of [ $^{14}\text{C}$ ]Mecoprop at Five Concentrations in Sub-surface Soil and in Sterilised Soil at  $5 \text{ mg kg}^{-1}$  Incubated for 211 days

Concn ( $\text{mg kg}^{-1}$ )	$^{14}\text{C}$ (%) ( $\pm \text{SD}$ )			Total recovery of $^{14}\text{C}$ (%) ( $\pm \text{SD}$ )
	KOH	Extract	Extracted soil	
0.0005	58.1 ( $\pm 12.0$ )	ND <sup>a</sup>	28.9 ( $\pm 8.6$ )	87.0 ( $\pm 13.5$ )
0.05	51.0 ( $\pm 0.8$ )	3.5 ( $\pm 0.0$ )	39.7 ( $\pm 1.1$ )	94.2 ( $\pm 1.1$ )
0.5	62.1 ( $\pm 0.05$ )	3.4 ( $\pm 0.3$ )	35.5 ( $\pm 1.7$ )	101.0 ( $\pm 1.2$ )
5	74.2 ( $\pm 0.0$ )	2.9 ( $\pm 0.0$ )	19.5 ( $\pm 2.3$ )	96.6 ( $\pm 2.6$ )
5, sterile	5.3 ( $\pm 0.6$ )	82.8 ( $\pm 1.3$ )	9.5 ( $\pm 2.5$ )	97.6 ( $\pm 2.3$ )
50	66.3 ( $\pm 2.2$ )	12.4 ( $\pm 1.3$ )	17.2 ( $\pm 3.4$ )	95.9 ( $\pm 3.5$ )

<sup>a</sup> ND = Not determined.

dioxide was negligible, and therefore a discussion of kinetics, at these high concentrations, is impossible.

The mineralisation rates at concentrations up to  $50 \text{ mg kg}^{-1}$  in the sub-surface soil progressed in almost the same way, but were delayed compared to in the surface soil (see Table 3). At 5 and  $50 \text{ mg kg}^{-1}$  in the sub-surface soil, a period of first-order kinetics was also seen, but it was not possible to show it statistically. At  $500 \text{ mg kg}^{-1}$  and higher concentrations, mineralisation was negligible.

### 3.3 Residue analysis and influence of sterilisation

After termination of the experiments, the soils were extracted and remaining  $^{14}\text{C}$  in the soil was determined by combustion. Total recovery of  $^{14}\text{C}$  ([ $^{14}\text{C}$ ]carbon dioxide in potassium hydroxide plus  $^{14}\text{C}$  extracted from the soil plus  $^{14}\text{C}$  found by combustion of the soils) is shown in Tables 4 and 5. The  $^{14}\text{C}$  in glycerol was only detectable in the surface soil at  $500 \text{ mg kg}^{-1}$ .

The recovery of the parent compound in soil extracts was, in most cases, below the limit of quantification for mecoprop ( $<6\%$ ). Between 20 and 50%  $^{14}\text{C}$  was not extractable and total recovery was between 83 and 111%.

There was almost no evolution of [ $^{14}\text{C}$ ]carbon dioxide from the sterilised soils, indicating that the degradation was microbial. About 63% and 83% of the  $^{14}\text{C}$  could be extracted from the surface and sub-surface soil, respectively, and all the  $^{14}\text{C}$  was identified as mecoprop by HPLC. The soil combustion showed that 31% and 10% was not extractable in the surface and sub-surface soil, respectively.

## 4 DISCUSSION AND CONCLUSIONS

Generally the shapes of the mineralisation curves are the same for surface and sub-surface soils, but the evolution is slower in sub-surface soil than in surface soil. The estimated time for 50% disappearance of mecoprop in the surface soil at concentrations up to  $5 \text{ mg kg}^{-1}$

(Table 2) is in the same order of magnitude as previously reported.<sup>5,7,10</sup> Tables 2 and 3 show that the evolution of [ $^{14}\text{C}$ ]carbon dioxide in sub-surface soil is only 12 to 17% of the evolution in surface soil. This result is not surprising, given that the size of the microbial biomass in most sub-surface soils is considerably smaller than in surface soils. Nevertheless, at the same concentration, the evolution of [ $^{14}\text{C}$ ]carbon dioxide from [ $^{14}\text{C}$ ]mecoprop can be described by the same equation at both depths.

Our observations of first-order kinetics at 0.0005, 0.05 and  $0.5 \text{ mg kg}^{-1}$  are in accordance with earlier published investigations, where first-order kinetics were found at  $0.05 \text{ mg kg}^{-1}$  MCPA and at  $0.05 \text{ mg kg}^{-1}$  2,4-D.<sup>13,14</sup>

At  $0.5 \text{ mg kg}^{-1}$  it was the linear form (eqn (1)) and at  $5 \text{ mg kg}^{-1}$  it was the exponential form (eqn (2)) of the three-half order model which gave the best fit. In the curves in Fig. 3 this appears as an increase in the mineralisation rate at  $5 \text{ mg kg}^{-1}$  following an initial constant degradation rate.

For both depths an increase in mineralisation rate was observed at 50 and  $500 \text{ mg kg}^{-1}$ . This pattern was followed by a decrease, corresponding with first-order kinetics, after most of the mecoprop was supposed to be degraded.

In another investigation, the linear form of the three-half order model was fitted to mineralisation data at  $10 \text{ mg kg}^{-1}$  2,4-D.<sup>14</sup> The difference in these observations is probably caused by the addition of 2,4-D-degrading micro-organisms and a higher temperature ( $22^\circ\text{C}$ ), which accelerated the degradation. It was also found that the exponential form fitted the mineralisation data at  $500 \text{ mg kg}^{-1}$  2,4-D.

As seen in Table 1, the sorption coefficients in the surface soil decrease when the concentration of mecoprop increases. This is probably due to filling of the sorption sites in the soil, so that an increase in mecoprop concentration increases the relative concentration in solution. The same connection between concentration and  $K_d$  was not seen in the sub-surface soil with very low  $K_d$  values.

Concentrations of 500 and 5000 mg kg<sup>-1</sup> are not unrealistic at point sources. There is an increased risk of leaching of mecoprop over an extended period of time when the herbicide originates from a point source, because there is no appreciable degradation of mecoprop at concentrations of 5000 mg kg<sup>-1</sup> and above in surface soil, or at 500 mg kg<sup>-1</sup> and above in sub-surface soil. There, the degradation is slow, and since sorption is low, mecoprop, even at lower concentrations, may be a threat to the ground water.

## 5 ACKNOWLEDGEMENTS

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